

REPORT

SUPPLEMENT TO
REPORT NO.

THIS IS UNEVALUATED INFORMATION

COOPER SMELTING IN KAZAKHSTAN

Prof V. A. Vanyukov

[Figures referred to herein are appended.]

Role of Central Kazakhstan

Before the Revolution, 50 percent of the copper smelting was carried on in the Urals, 25 percent in the Caucasus, about 12 percent in Siberia, and the rest in other regions.

At present, Kazakhstan is replacing the Urals as the copper-smelting center, although the Urals still contribute a large amount of smelted copper to all-Union production.

There are enormous copper reserves in Central Kazakhstan. They are described in "Bolshoy Dzherkazgan," Trudy Kazakhstanskoy Bazy Akademii Nauk SSSR (Works of the Kazakhstan Base, Academy of Sciences USSR), 1935, No 7: N. P. Mirovortsev, pp 19 - 32; M. P. Rusakov, *ibid.*, pp 33 - 84; and K. I. Saipayev, *ibid.*, pp 195 - 257. The Kounrad and Bashchekul' deposits contain porphyritic ore; the Dzherkazgan deposit contains sheet-like ore. These deposits made it practical to build the large Balkhash, Bolshoy Dzherkazgan, and other copper smelting plants. Since Central Kazakhstan copper ores contain little sulfur, it is advantageous to use them instead of the pyritic ores which contain from 40 to 44 percent sulfur. The latter are a great economic asset for the sulfuric acid industry of the USSR.

The change to utilization of Kounrad and Dzhezkazgan ores was planned to conform with development of the Soviet copper industry. The Kounrad deposit became known rapidly as a result of extensive prospecting, and subsequently it became the foremost among the newly developed deposits. After the Kounrad deposit, the Dzhezkazgan is the next main deposit to be exploited.

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Distinctive Composition of Ores and Concentrates

The copper ores of Central Kazakhstan and the concentrates obtained from them differ sharply in composition from ores being smelted in the Urals. Therefore, the practical experience gained in the Urals could not be applied directly in Central Kazakhstan.

Central Kazakhstan ores contain 60 - 67 percent silica, 9.6 - 15.5 percent alumina, 2.8 percent iron, and 0.95 percent sulfur.

The concentrate also differs sharply from Ural concentrate and from concentrate being produced abroad. It consists of 35 - 40 percent silica, 6 - 9 percent alumina, 7 - 10 percent iron, 2 - 3 percent lime, and 12 - 18 percent sulfur.

In the Dzhezkazgan region, in addition to iron fluxes there are manganese and iron-manganese ores which can be used as fluxes. Since 1943, in the course of manganese ore mining for ferrous metallurgy, tailings have accumulated which can be used as fluxes since they contain manganese oxide.

In 1928, V. A. Vanyukov proposed that these valuable components of ores and concentrates be used and that smelting of Dzhezkazgan ores and concentrates be carried on with the goal of obtaining, first, highly siliceous manganese slag and, secondly, super-rich matte.

The iron-manganese flux is valuable because during smelting of siliceous ore the manganous oxide enters the slag, makes the ore more readily smeltable, and reduces the viscosity of the slag. It was also found that this property of manganous oxide could be used most advantageously to process the waste slag which resulted from smelting Dzhezkazgan sulfide ore by the reverberatory method.

The opinions of Professors V. A. Vanyukov and I. P. Zaleskiy, in an expert appraisal of the Karsakpay plant project, led to a proposal to work for a 60 - 65 percent copper matte, because a system of upright converters, which did not permit preheating, existed at the plant.

First Experimental Melts

The administration of the Atbasar Trust began to conduct extensive tests on a laboratory and greater-than-laboratory scale. Prof V. A. Vanyukov, of the Moscow Mining Academy, was entrusted with the carrying out of these tests.

The Atbasar Trust sent average samples of sulfide, oxidized ore, coal, iron and iron-manganese ore, and limestone. At that time there was no concentrate, the concentrating plant having been planned to begin operations in May 1929. Until the concentrating plant began operations, the experimental Karsakpay plant had to use sulfide ore for smelting. The tests, the results of which are shown in Tables 1 and 2, had for the most part been completed when the experimental Karsakpay plant began operations.

Experimental melts in the laboratory furnace with 8 - 10 percent pyrite added to the charge produced 50 percent matte. This indicated that in order to obtain 60 percent matte, the pyrite admixture would have to be completely eliminated.

Thus it was shown that because of the unusual composition of Central Kazakhstan (Dzhezkazgan and Kounrad) ores and concentrates, their components are valuable parts of the charge and therefore ought to be used. Hence it was expedient to carry on smelting so as to obtain 60 percent, or higher, mattes, and acid manganese slag with 54 - 58 percent SiO_2 content.

Smelting at Karsakpay

At first, smelting at Karsakpay was carried on in accordance with foreign practice. In view of the extensiveness of the Dzhezkazgan deposit, the Karsakpay plant was considered an experimental plant for a large plant of the future.

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The Karsakpay Copper Smelting Plant was the first of the new nonferrous metallurgical plants in the Soviet Union to be built according to a plan for concentrating the ore and smelting the flotation concentrate in reverberatory furnaces.

When the plant went into operation, the concentrating plant had not yet been completed, and this was the reason for smelting the rich sulfide ore first.

The high silica and alumina and low iron content of the ore was a favorable and not unfavorable factor, as some metallurgists at first thought. To a great extent the latter attitude delayed adoption of the new method of smelting ores and concentrates so as to obtain highly siliceous slag and super-rich matte.

"Logiprotvetmet" (Leningrad Section, State Planning Institute for Nonferrous Metallurgical Plants) wrote, in the final plan of the Karsakpay plant, "Because of the difficulty and even impossibility of operating the plant so as to obtain 60-percent matte, we must work out the copper by adding pyrite to the charge. According to the data of literature, the blowing of even 55 percent matte in the converter requires the application of special processes. For normal operations in Karsakpay, we consider it possible to have a 50 percent copper content in the matte."

"Logiprotvetmet" gave the slag composition as 40.4 percent SiO_2 , 35.25 percent FeC , 4.9 percent CaO , 0.7 percent MgO , 8.5 percent Al_2O_3 , and 0.45 percent Cu .

Table 3 shows that the charge was overloaded with fluxes.

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Table 1. Crucible Melts of Dzhezkazgan Sulfide Ore

Melt No	Composition of Charge Material	Amount (g.)	(% of ore wt)	Products Obtained (wt in gr)	Cu	Chemical Composition (%)		
						SiO ₂	Fe ₂ O ₃ + Al ₂ O ₃	CaO
1.	Sulfide ore	1,600	100	Matte	55.8	--	--	--
	Hematite	800	50					
	Limestone	320	20	Slag	0.55	59.36	29.76	7.92
	Pyrite	96	6					
2.	Sulfide ore	1,600	100	Matte	29.07	--	--	--
	Iron ore	590	37					
	Limestone	320	20	Slag	0.47	57.56	29.04	8.20
	Pyrite	320	20					
3.	Sulfide ore	1,600	100	Matte	33.03	--	--	--
	Iron ore	590	37					
	Limestone	320	20	Slag	--	--	--	--
	Pyrite	320	20					
4.	Sulfide ore	1,600	100	Matte	44.56	--	--	--
	Hematite	800	50					
	Limestone	320	20	Slag	0.25	58.03	31.20	9.20
	Pyrite	240	15					
5.	Sulfide ore	1,600	100	Matte	31.21	--	--	--
	Hematite	342	21					
	Limestone	160	10	Slag	--	--	--	--
	Pyrite	320	20					

Remarks

- Melt 1. Slag rather viscous, flowed freely from crucible
- Melt 2. Slag good, flowed freely; matte separated satisfactorily from slag. Addition of 20 percent pyrite is large.
- Melt 3. Slag good. Addition of pyrite is large.
- Melt 4. Slag liquid, breaks well.
- Melt 5. Object was to obtain more acid slag. Slag not as good as previously. Slag not analyzed. Addition of pyrite is large.

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Table 2. Melts in Laboratory Reverberatory Furnace

Melt No.	Composition of Charge		Products Obtained	Cu	Chemical Composition			
	Material	Amount			SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	CaO
		(kg) (% of ore wt)						
1.	Sulfide ore	200	Matte	49.21	--	--	--	--
	Hematite	37						
	Limestone	37	Slag	0.41	62.0	23.52	5.30	
	Pyrite	16						
2.	Sulfide ore	200	Matte	52.54	--	--	--	--
	Hematite	64						
	Lime	32	Slag	0.45	52.80	30.32	8.11	
	Pyrite	16						
3.	Sulfide ore	150	Matte	54.45	--	--	--	--
	Atbasar iron ore	30						
	Manganese ore	30	Slag	0.39	50.48	39.80	6.4	
	Atbasar lime-stone	37.5						
	Pyrite	15						

Remarks

Melt 1. Temperature in smelting space of furnace 1,420 degrees.

Melt 2. Temperature in smelting space of furnace 1,450 degrees, temperature of bath 1,340 degrees. Separation of matte and slag better. Slag thinner than in melt No 1.

Melt 3. This test was a check on tests No 1 and 2, conducted with local fluxes. Temperature of bath 1,240 - 1,300 degrees. Time of melt 6 hours, 45 minutes. Temperature of slag when flowing off 1,240 degrees. Slag flowed off well. Matte separated well from slag.

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Table 3. Smelting of Sulfide Ore

Composition of Charge (material)	(% of charge)	(with ore equal to 100%)	(matte)	Product (slag)
First Phase of Melt Using Ore Only, March 1929				
Sulfide ore	58.60	100.0	43 Cu	--
Iron ore	21.57	36.82	--	40.5 SiO ₂
Limestone	12.17	20.85	--	35.25 FeO
Pyrite	7.64	13.02	--	14.60 CaO 0.7 MgO 8.5 Al ₂ O ₃ 0.45 Cu
First Phase of Melt Using Ore and Concentrate, July 1930				
Concentrate	36.2	66.17	45 Cu	--
Sulfide ore	18.5	33.83	--	41.7 SiO ₂
Iron ore	16.3	29.79	--	30.15 FeO
Limestone	12.6	23.03	--	12.30 CaO
Pyrite	16.4	29.98	--	7.54 Al ₂ O ₃ 0.76 MgO 0.45 Cu

Smelting of Sulfide Ore and Concentrate

At the third session of the Scientific Council of the Kazakhstan Section, Academy of Sciences USSR, which was devoted to the problems of Bol'shoy Altay and Bol'shoy Dzhezkazgan combines, Prof V. A. Vanyukov reported the smelting of Central Kazakhstan sulfide ores and concentrates. This report is recorded in "Bol'shoy Dzhezkazgan," Trudy Kazakhstanskoy Pazy Akademii Nauk SSSR, 1935, No 7, pp 517 - 531.

In 1928, the experimental Karsakpay Copper Smelting Plant had been operating for 6 years. It was already experimenting with the new method and trying to adapt it to production.

I. A. Strigin stated in a paper "Bol'shoy Dzhezkazgan" on the smelting of Dzhezkazgan copper ore, published in Trudy Kazakhstanskoy Pazy Akademii Nauk SSSR, 1935, No 7, pp 435 - 462, that at first the plant followed a policy of copying the developments in other plants. In the early period of its operation, a shortage of sulfur was compensated for by adding pyrite to the charge, and the plant administration familiarized itself with working with 45-percent copper matte. But, getting pyrite from the Urals was difficult. In August 1930, under the supervision of V. P. Istomin and I. P. Pomin, plant metallurgists, the amount of pyrite in the charge was reduced, and the results indicated the possibility of almost completely eliminating pyrite from the charge. Without much difficulty, they mastered the production of 60 - 52 percent matte, obtained as a result of smelting without the addition of pyrite to the charge. Thus, the method of obtaining 60-percent copper matte, proposed by Prof V. A. Vanyukov, was mastered by the Karsakpay plant.

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The proposal of the author to carry on smelting so as to obtain slag containing more than 50 percent SiO_2 and only 4 - 8 percent calcium oxide was also adopted and eventually produced altogether satisfactory results. The resultant slags were adequately fluid and clean of copper.

These events provided the author with the opportunity of expanding the proposal which he had made in regard to the Balkhash Combine, namely, to operate it from the very beginning so as to obtain white metal and highly siliceous slags. His proposal also applied to the operations of the giant copper-smelting plant in Dzhezkazgan.

In the processing of ore at the Bolshoy Dzhezkazgan Plant, the crushing and grinding is followed by the first flotation and recovery of the first concentrate. The second flotation results in a rich concentrate which is smelted to obtain super-rich matte, ranging up to white metal, with a minimum admixture of iron-manganese ore and limestone. The resulting super-rich matte (62 - 79 percent Cu) is Bessemerized, with preheating of the converter, to yield Bessemer copper (99.6 percent Cu). The slag formed in the smelting process contains 54 - 58 percent SiO_2 with 0.2 to 0.4 percent Cu, a recovery of 97 to 98.5 percent

The advantages of this ore-processing method include:

1. Lower electric power consumption in crushing
2. High operating capacity of the flotation machines
3. High recovery of copper (97 - 98.5 percent)
4. Minimum consumption of fluxes to obtain slag containing 54 - 58 percent SiO_2 .
5. Maximum utilization of furnace sole
6. Normal consumption of fuel (coal ought to have 8 - 10 percent ash content)
7. Lean slag residue
8. Less converted slag (none during first stage of Bessemerizing)
9. Lower capital investment
10. Lower operating costs

These advantages permit the production of cheaper copper because it can be more completely recovered. As a result, the process is being perfected.

Prof Vanyukov's report received the full approval of the Scientific Council. Academy Member A. A. Baykov said: "I think that the way in which the research work of the Combine was conducted was perfectly correct. In regard to smelting in the reverberatory furnace, it was essential to change to a strongly acid slag containing up to 60 percent SiO_2 . The proposed method of obtaining manganese slag yields good results. I think that if matte with a 70 - 60 percent Cu content is obtained, that will be satisfactory."

A resolution of the session reads: "The session states that the following main features in the method of processing Dzhezkazgan ore must be accepted: (1) smelting to obtain slag as acid as the nature of Dzhezkazgan ore requires; (2) smelting to obtain super-rich matte; Bessemerizing of rich matte; and (3) adding iron-manganese fluxes to the charge in reverberatory smelting."

The session of the Academy of Sciences recommended that the following projects in metallurgical processes be carried out:

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1. Study of the hydrometallurgical method of processing oxidized copper ores
2. Study of a method of smelting mixed oxidized and sulfide concentrates
3. Study of the physical properties of highly siliceous slags containing manganous oxide and alumina
4. Study of the white-metal slag equilibrium system, from the point of view of copper going over into the slag
5. Study of the nature and properties of super-rich matte in connection with manganese slag
6. Study of ferrite formation in connection with the Bessemerizing of super-rich mattes
7. Smelting of concentrates in plants to obtain white metal and super-rich matte
8. Study of Bessemerizing of super-rich mattes and white metal.
9. Experimental work in direct reduction of Dzhezkazgan iron ores

All of these projects were fully carried out by Prof. V. A. Vanyukov and his students.

Highly Siliceous Slag

Here we shall look at problems connected with the slag formed in smelting the highly siliceous Central Kazakhstan ores and concentrates, which has a high alumina and a low ferrous oxide content.

Such slag from reverberatory smelting was obtained for the first time in the Soviet Union by the author. Foreign practice and literature are not acquainted with this kind of slag.

The main problem was to establish a maximum silica content in slag which also had a 10 - 12 percent Al_2O_3 content.

World practice of reverberatory copper smelting has held up to now that a 42-percent SiO_2 content in slag (Anacosta Plants, USA) was the maximum compatible with the viscosity of such slag. Even at high temperatures, such slag does not flow readily. Draining the slag from the furnace is troublesome. Losses of copper occur. The smelting capacity of the furnace is reduced. The presence of alumina in acid slag increases its viscosity still more.

While carrying on work in copper slags, described in Metallurgie, 1912, pp 1 - 27, 48 - 62, Prof. V. A. Vanyukov studied the question of substituting manganous oxide for ferrous oxide in slags and pointed out that manganous oxide considerably thins slags with a high silica content. This discovery enabled him to propose to the Atbasar Trust, in 1927, that Dzhezkazgan ores and concentrates be smelted in the reverberatory furnace so as to yield highly siliceous manganese slag.

Experiments carried out in a laboratory and on a larger scale have shown that it is possible to employ slag containing 54 - 58 percent SiO_2 , 29 - 31 percent Fe_2O_3 + Al_2O_3 , and 8.20 - 9.10 percent CaO. See Tables 1 and 2.

Equilibrium System: Mattes of Varying Composition, Acid Slag Containing Manganese

In 1935, the author and V. G. Kirillov made a study of equilibrium systems which was published "Sostav i Svoystva Normal'nykh i Sverkhbogatykh Shteynov pr. Zhelezo-

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Margantsovistom Shiak" (Composition and Properties of Normal and Super-Rich Mattes in Connection With Iron-Manganese Slag) in Iubileyny Sbornik Nauchnykh Trudov Kafedry Tvezhelykh Metallov MITSMLZ (Jubilee Edition of the Scientific Works of the Heavy Metals Desk of the Moscow Institute of Nonferrous Metals and Gold); 1939, No 7. It was a study of highly siliceous slag mattes (composed of 55 percent SiO_2 , 15 percent Al_2O_3 , 5 percent MnO) of varying composition, containing 20, 30, 40, 50, 55, 60, 65, and 75 percent Cu. See Figure 1.

Table 4 and Figure 1 show that when 30 - 40 percent matte is obtained from smelting, only 0.07 percent Cu goes over into the highly siliceous slag; when 50 - 60 percent matte is obtained, only 0.09 - 0.15 percent Cu; and when 60 - 79 percent matte is obtained, only 0.15 - 0.25 percent Cu goes over into the slag.

Table 4. Composition of Mattes and Copper Content in Slag (%)

Test No.	Cu	Composition of Mattes				Copper Content in Slag
		Fe	S	Mn	Unanalyzed	
1	20.69	45.22	29.20	0.51	4.38	0.05
2	30.86	36.09	27.56	0.26	4.58	0.07
3	41.39	29.67	26.87	0.89	1.18	0.07
4	52.92	19.68	24.68	0.64	2.18	0.12
5	56.80	16.83	24.27	0.26	1.84	0.15
6	62.33	12.81	23.80	0.64	0.42	0.15
7	66.53	9.12	23.09	0.32	0.94	0.20
8	70.61	4.85	22.72	0.28	1.74	0.22
9	74.83	4.42	19.92	0.16	0.67	--
10	79.86	0.21	19.66	0.14	0.13	0.25

The addition of 5 percent MnO to the composition of highly siliceous slag reduced its viscosity.

Figure 2 presents a comparison of the data of the author with the data of Grabill, Engineering and Mining Journal, 1910, p. 776, who studied copper losses in connection with the usual iron-lime composition of slag; 31.04 percent SiO_2 , 51.40 percent FeO , 4.84 percent Al_2O_3 , 6.30 percent CaO , 1.37 percent MgO , 1.36 percent S, 2.01 percent Zn, 0.51 percent Mn, and 0.45 percent Cu.

The curve obtained by the author shows a considerably lower copper content in slag than does Grabill's curve. Grabill's curve shows that it is unprofitable to work with matte containing more than 40 - 45 percent Cu, since from this point on the copper going over into the slag increases considerably. The author's curve, however, shows the contrary. Thus, the norms established by foreign practice were broken. It was also shown that by adding a small amount of manganese oxide, cleaner slag could be obtained than in foreign practice.

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Compositional Change in Mattes

When adding iron-manganese ore to the smelting charge, it is important to know how the manganese reacts on matte elements and to what extent the manganese goes over into the matte.

Mattes were prepared containing 20, 30, 40, 50, 60, 65, 70, and 75 percent copper and white metal. They were obtained by two series of tests:

First series -- resmelting of mattes in graphite crucibles under a thick layer of charcoal.

Second series -- resmelting of the mattes obtained in the first series in intimate mixture with a charge calculated to yield highly siliceous manganese slag containing 55 percent SiO_2 , 15 percent Al_2O_3 , 5 percent CaO , 20 percent FeO , and 5 percent MnO .

After having been smelted, the contents of the crucibles were mixed with a carbon rod and gradually cooled. (See Tables 5 and 6).

Table 5. Composition of Mattes, First Series of Tests (%)

Test No	Cu	Fe	S	Insoluble Residue
1	19.88	47.19	29.74	1.51
2	30.02	39.66	28.25	1.67
3	40.05	31.63	26.62	1.62
4	50.20	22.59	24.95	1.32
5	56.22	19.58	23.53	0.57
6	60.24	13.07	22.27	0.33
7	65.78	9.04	20.40	0.28
8	70.78	9.04	20.37	0.28
9	75.30	4.52	19.91	0.22
10	79.86	0.08	20.09	--

Table 6. Composition of Mattes, Second Series of Tests (%)

Test No	Cu	Fe	S	Mn	Unanalyzed
1	20.69	45.22	29.20	0.51	4.38
2	30.86	36.09	27.56	0.96	4.53
3	41.39	29.67	26.97	0.89	1.18
4	52.92	19.68	24.68	0.64	2.18
5	56.80	16.83	24.27	0.26	0.84
6	62.33	12.81	23.80	0.64	0.42
7	66.53	9.12	23.09	0.32	0.94
8	70.61	4.85	22.72	0.28	1.74
9	74.83	4.42	19.92	0.16	0.67
10	79.86	0.21	19.66	0.14	0.13

The mattes of the first series of tests underwent little change (only those below 75 percent Cu). The mattes of the second series underwent great change:

1. The copper content increased in all mattes below 70 percent Cu.
2. The iron content in the same mattes decreased.

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3. The sulfur content in all mattes decreased, except mattes with 60, 65, and 75 percent Cu.

4. The manganese content in mattes containing less than 75 percent Cu varied from 0.28 to 0.96 percent; 75 percent Cu mattes contained 0.16 percent Mn; and white metal contained 0.14 percent Mn.

Figure 3 illustrates the amount of manganese carried over into the matte in relation to copper content.

The manganese carried over into the matte is insignificant; therefore, we can effectively use small amounts of iron-manganese ore as a flux.

Effect of Manganous Oxide on Viscosity of Acid Slag

In 1935, Prof V. A. Vanyukov and Engineer I. F. Kvaakov studied the viscosity of highly siliceous slags obtained in connection with smelting white metal. They used the falling ball method described by F. M. Loskutov, Puti Snizheniya Soderzhaniya Med1 v Otval'nykh Shlakakh (Ways of Reducing Copper Content in Waste Slag); ONTI, 1935, p 16.

The absolute viscosity was computed according to the formula of Stokes as corrected by Landenburg, which measures the effect of viscosity on the walls of the crucible and on the upper and lower fusion surfaces in the crucible.

Three groups of slag were studied.

In the first group of tests, the goal was to have enough manganous oxide in the slag to assure getting a liquid slag. With the original slag containing 55 percent SiO_2 , 32 percent FeO , 5 percent CaO , and 8 percent Al_2O_3 , an equivalent amount of manganous oxide was gradually substituted for the ferrous oxide. The viscosity was measured every 50 degrees of temperature between 1,450 and 1,150 degrees. (See Table 7 and Figure 4.)

The following results were established:

1. Substituting manganous oxide for ferrous oxide sharply reduces the viscosity of slag (3 times at 1,250 degrees).
2. This reduction is sharply noticeable when $1/4$ FeO and $1/2$ FeO has been replaced. At 1,200 degrees, viscosity drops from 4,000 to 2,400 poise. At 1,250 degrees, viscosity drops, respectively, from 2,130 to 1,130 and 910 poise when $1/4$ and $1/2$ FeO has been replaced by MnO . Upon further substitution of MnO for FeO ($3/4$ and $4/4$), viscosity at 1,250 degrees does not drop very much -- to 810 and 720 poise -- and this slight fall is of no interest. Since a 1,200-degree temperature in the reverberatory furnace is customary for ordinary iron slag, for highly siliceous slag it must be 1,250 degrees.
3. At higher temperatures, the viscosity of slag drops rapidly and, therefore, substitution of manganous oxide for ferrous oxide is less effective in reducing viscosity. At 1,450 degrees, the viscosity is 100 poise.

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Table 7. Effect of Substituting Manganous Oxide for Ferrous Oxide on the Composition and Viscosity of Slag

Slag No	SiO ₂	Composition FeO		MnO	CaO	(%) Al ₂ O ₃	Cu	Poise (viscosity at 1,250°)
		(remaining)	(replaced)					
1	55.0	32.0	0	0	5.0	8.0	0.72	2,130
2	55.0	24.0	1/4	8.0	5.0	8.0	0.41	1,130
3	55.0	16.0	1/2	16.0	5.0	8.0	0.32	910
4	55.0	8.0	3/4	24.0	5.0	8.0	0.15	810
5	55.0	0.0	4/4	32.0	5.0	8.0	0.12	720

In the second group of tests, the goal was to study the effect on slag viscosity of substituting an equivalent amount of calcium oxide for the ferrous oxide. The tests were conducted with slag containing 55 percent SiO₂, 24 percent FeO, 8 percent MnO, 5 percent CaO, and 8 percent Al₂O₃. See table 8, slag No 2. In addition, 1/4, 1/2, 3/4, and 4/4 substitutions of Fe for CaO were made. (See Table 8 and Figure 5.)

The following results were established:

1. Slag containing manganous oxide and 2.0 percent CaO has a viscosity of 220 poise at 1,250 degrees.
2. The viscosity increases somewhat with 3/4 and 4/4 substitution of calcium oxide for FeO.
3. The viscosity of slag containing manganous oxide and calcium oxide drops to 50 poise at 1,450 degrees. The viscosity of the initial slag (slag No 2) at this temperature is 100 poise.

Table 8. Effect of Substituting Calcium Oxide for Ferrous Oxide on Composition and Viscosity of Slag No 2

Slag No	SiO ₂	Composition FeO		CaO	(%) Al ₂ O ₃	MnO	Poise (viscosity at 1,250°)
		(remaining)	(replaced)				
2	55.0	24.0	--	5.0	8.0	8.0	1,120
6	55.7	18.2	1/4	9.9	8.1	8.1	220
7	56.5	12.4	1/2	14.7	8.2	8.2	210
8	57.3	6.3	3/4	19.8	8.3	8.3	320
9	58.1	0.0	4/4	25.1	8.4	8.4	330

In the third group of tests, the effect on slag viscosity of adding 4, 8, 12, and 16 percent Al₂O₃ to the slag was studied. The tests were conducted with slag containing 55 percent SiO₂, 24 percent FeO, 8.0 percent MnO, 5 percent CaO, and 8 percent Al₂O₃. See Table 9, Slag No 2.

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The following was established:

1. The viscosity of the slag rose sharply as alumina was added.
2. Notwithstanding respective viscosity measurements of 1,150 and 1,490 poise with 11.5 and 14.8 percent Al_2O_3 content, the copper content was 0.24 and 0.23 percent, respectively. With 17.8 percent Al_2O_3 content and 2,200 poise viscosity measurement, the copper content was 0.42 percent.

Table 9. Effect on Viscosity of Adding Alumina to Slag No 2

Slag No	Composition of Slag Before and After Addition (%)						Poise	
	SiO ₂	FeO	Al ₂ O ₃ (was)	Al ₂ O ₃ (added)	CaO	MnO	Cu	(viscosity at 1,250°)
2	55.0	24.0	8.0	--	5.0	8.0	0.41	1,120
10	55.0	24.0	8.0	4.0	5.0	8.0	0.24	1,150
	52.9	23.1	11.5	--	4.8	7.7	--	--
11	55.0	24.0	8.0	8.0	5.0	8.0	0.23	1,490
	50.9	22.2	14.8	--	4.6	7.5	--	--
12	55.0	24.0	8.0	12.0	5.0	8.0	0.42	2,220
	49.1	21.4	17.8	--	4.5	7.2	--	--
13	55.0	24.0	8.0	16.0	5.0	8.0	0.96	2,670
	47.4	20.7	20.7	--	4.3	6.9	--	--

The content of manganese oxide must be cut from 8 to 2 percent for minimum copper carry-over in slag-containing MnO, as was determined by the author at the Karsakpay experimental plant. See Table 10.

Table 10. Effect of Manganese Oxide on Reducing Copper Content in Highly Siliceous Slags (Matte Containing 54% Cu Used in These Tests)

Time of Test	Composition					(%)
	Cu	SiO_2	FeO	CaO	Al_2O_3	MnO
Aug 1935	0.67	53.60	21.24	2.57	11.94	none
	0.83	54.32	18.85	3.80	12.22	none
	0.93	56.02	18.83	3.80	13.06	none
	1.10	61.00	14.59	4.84	12.36	none

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Time of Test	Cu	SiO ₂	Composition		Al ₂ O ₃	MnO (%)
			FeO	CaO		
Sep 1935	0.45	56.52	16.86	4.37	12.27	0.65
	0.27	57.60	14.80	3.60	12.92	0.88
	0.30	54.20	14.85	3.28	14.81	2.09
	0.28	55.64	14.26	3.61	12.26	2.18

The copper content in highly siliceous slag is considerable, 0.67 - 1.1 percent, when there is no manganous oxide in it. See Table 10. It increases with a rise in alumina content. Also, rising slag viscosity has a great effect on copper losses.

After manganous oxide has been added to the slag, the copper content becomes less. For example, the presence of from 0.88 to 2.18 percent MnO cuts copper content in the slag from 0.27 to 0.28 percent. Such slag is wholly waste and permits the recovery of up to 98.57 percent Cu. The slag is quite fluid and can be drained freely from the reverberatory furnace.

Melting Temperatures of Acid Slags

V. A. Vanyukov and V. Ya. Korolyuk studied the melting temperature, specific gravity, and other properties of highly siliceous slag containing manganous oxide and alumina. See "Izucheniye Fizicheskikh Svoystv Vysokokremistykh Shlakov s Soderzhaniyem Zakisi Manganosa i Glinotsoma" (Study of the Physical Properties of Highly Siliceous Slags Containing Manganous Oxide and Alumina) in Yubileyny Sbornik Nauchnykh Kafedry Tsvetnykh Metallov MITU (Jubilee Edition of the Works of the Heavy Metals Desk of the Moscow Institute of Nonferrous Metals and Gold), No 7, 1939, pp 136 - 142.

These data were indispensable for determining the optimum composition of highly siliceous slag in smelting Central Kazakhstan ores and concentrates.

Pure original materials, prepared in the heavy metals laboratory of "Mintsvetmetzoloto" (Moscow Institute of Nonferrous Metals and Gold), were used to obtain the slag. Smelting was done in Morgan "G" chamotte crucibles in an oil furnace.

After the crucible charge had melted, it was removed while hot from the furnace and cooled.

Crucibles with a charge of a specific group were placed in the furnace under identical temperature conditions.

All charges were divided into the following groups:

1. Iron slag containing from 45 to 60 percent SiO₂
2. Slag containing 55 percent SiO₂, in which ferrous oxide had been replaced with manganous oxide.
3. Same as group 2 but containing 60 percent SiO₂
4. Slag containing 55 percent SiO₂, in which 1/2 FeO had been replaced with manganous oxide; calcium oxide added

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5. Slag containing 55 percent SiO_2 , in which $1/4$ FeO had been replaced with manganous oxide; alumina added

6. Slag containing 55 percent SiO_2 , in which $1/4$ FeO had been replaced with manganous oxide; calcium oxide and alumina added

A total of 21 specimens of slag were prepared. (See Table 11).

Table 11. Composition of Slags (%)

Group	Slag No	SiO_2	FeO	MnO	CaO	Al_2O_3	Total
1	1	45	45.0	0.0	6	4	100
	2	50	40.0	0.0	6	4	100
	3	55	35	0.0	6	4	100
	4	60	30	0.0	6	4	100
2	5	55	26.25	8.75	6	4	100
	6	55	17.5	17.5	6	4	100
	7	55	8.75	26.25	6	4	100
	8	55	0.0	35.0	6	4	100
3	9	60	22.5	7.5	6	4	100
	10	60	15.7	15.0	6	4	100
	11	60	7.5	22.5	6	4	100
	12	60	0.0	30.0	6	4	100
4	13	55	26.25	8.75	6 6	4	100 6
	14	55	26.25	3.75	6 12	4	100 12
	15	55	26.25	8.75	6 18	4	100 18
5	16	55	26.25	8.75	6	4 4	100 4
	17	55	26.25	8.75	6	4 8	100 8
	18	55	26.25	8.75	6	4 12	100 12
6	19	55	26.25	8.75	6 6	4 4	100 10
	20	55	26.25	8.75	6 12	4 8	100 20
	21	55	26.25	8.75	6 18	4 12	100 30

An attempt to determine the melting temperatures of these acid slag specimens by taking down cooling curves was not successful. Therefore, to determine the formation temperatures, cones were prepared from the charges which were used to obtain the slags shown above. The slags obtained were ground up to 250-mesh size granules and from them, likewise, cones were prepared.

Slag formation temperatures (charge cone) and slag melting temperatures (slag cone) were determined with the aid of a thermocouple in the muffle and by observing the temperature at which the apex of a cone began to fold. (See Table 12.)

Table 12. Slag Formation and Melting Temperatures ($^{\circ}\text{C}$)

Melt No	Formation Temperature	Melting Temperature
1	1,210	1,110
2	1,240	1,130
3	1,270	1,160
4	1,300	1,190
5	1,170	1,130
6	1,160	1,115

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<u>Melt No</u>	<u>Formation Temperature</u>	<u>Melting Temperature</u>
7	1,155	1,120
8	1,160	1,150
9	1,200	1,170
10	1,200	1,160
11	1,210	1,170
12	1,210	1,180
13	1,140	1,120
14	1,130	1,110
15	1,125	1,115
16	1,190	1,160
17	1,185	1,150
18	1,180	1,150
19	1,160	1,115
20	1,130	1,110
21	1,125	1,100

The table shows that:

1. Iron slags containing from 45 to 60 percent SiO_2 (first group) have slag-formation temperatures of from 1,210 to 1,300 degrees, and slag-melting temperatures of from 1,110 to 1,190 degrees. These slags are not very satisfactory because of their high formation temperatures and also their viscosity, which usually necessitates much superheat.
2. Iron-manganese slags containing 8.75 - 35 percent MnO and 55 percent SiO_2 (second group) have considerably lower formation temperatures, 1,170 - 1,155 degrees. The melting temperatures of these slags are also lower, 1,115 - 1,150 degrees. These slags are fully acceptable and have a comparatively low viscosity. Replacement of even $1/4$ FeO with manganous oxide results in a good slag.
3. Iron-manganese slags containing 7.5 - 30 percent MnO and 60 percent SiO_2 (third group) have higher temperatures of formation, 1,200 - 1,210 degrees and melting, 1,180 - 1,160 degrees. Therefore, they require much superheat. These slags can be used when good metallurgical fuel is available.
4. Addition of calcium oxide up to 24 percent and alumina up to 16 percent to slags consisting of 55 percent SiO_2 , 26.25 percent FeO , and 8.75 percent MnO (fourth-sixth groups) reduces both slag formation and melting temperatures. These admixtures are satisfactory and make the slag liquid. The addition of mixtures is especially satisfactory.
5. The slags of all groups are vitreous and have a conchoidal fracture after rapid cooling, lithoidal fracture after slow cooling. The color of the slags is black, with a reddish hue when manganous oxide is present.

Main Aspects of Slag Formation for Reverberatory Smelting of Central Kazakhstan Ores and Concentrates

Prof. V. A. Vanyukov and his students in the Moscow Mining Academy and "Mintsvetmetzoloto" have demonstrated the following:

1. High silica and alumina content in ore and concentrate is not a negative factor; it is possible to minimize their effect of causing higher slag viscosity by adding a small amount of iron-manganese ore, which is being mined in the Dzhezhkagan region. Thus, all the conditions exist for obtaining slag free of copper content. The necessity for importing iron fluxes is eliminated. The size of the charge is reduced, a factor which cuts down considerably on the number of smelters needed.

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2. The small amount of iron in the ore and concentrates is also favorable for obtaining clean slag and a high rate of copper recovery.

3. Addition of the lacking amount of calcium oxide cuts down on copper content in slag. Therefore, the following composition of waste slag from smelting of Central Kazakhstan ores and concentrates can be set up as ideal: 52 - 58 percent SiO_2 , 16 - 20 percent FeO , 8 - 13 percent Al_2O_3 , 4.8 percent CaO , and 0.88 - 2 percent MnO .

Introduction of the Method of Smelting Kazakhstan Ore Concentrates to Yield Rich Matte and Highly Siliceous

In 1931, a very serious project was undertaken at the Karsakpay plant. This project radically changed the situation existing when metallurgists adhered to the smelting process which produced slag of the same type as that obtained in American plants.

The position of the plant in regard to fluxes obliged the Trust Administration to adopt the proposal of Engineer A. P. Ivanov and, in July 1931, to convert to a more acid slag, containing 52 percent SiO_2 , 20 percent FeO , 12 percent CaO , and 13 percent Al_2O_3 .

A. P. Ivanov carried on tests with acid slag from August 1931 to July 1932. At the same time, a project to obtain matte containing 60 percent Cu was being carried on.

The new method of "forced" smelting was carried forward in 1934.

In the summer of 1933, limestone was discovered in the immediate vicinity of the plant.

At the suggestion of K. V. Sushkov, a charge was computed to yield a most acid iron slag and rich matte.

Work was carried on with matte containing 60 percent Cu. In May, slag was obtained containing 0.51 percent Cu, in June 0.44 percent Cu, and in July 0.42 percent Cu.

The work of Engineer K. V. Sushkov, also that of Engineer A. P. Ivanov, was "forced" and his solution one-sided. Though his criticism of the large calcium oxide content in the experimental slags of A. P. Ivanov was correct, Sushkov's view of having only ferrous oxide content in slag was incorrect. He also overlooked the effect of manganous oxide on reducing copper content in slag.

Six years' work on the problem of selecting slags and smelting conditions enabled Chief Engineer I. A. Strigin to state the following conclusion in regard to the work of the experimental Karsakpay plant, towards the end of 1934.

1. Acid slags containing up to 52 percent SiO_2 are the most economical for processing the siliceous ores and concentrates of the Dzhezkazgan deposit.
2. Bessemerizing of rich mattes, containing up to 62 percent Cu, is technically possible and has been practically demonstrated.

By the end of 1934, the proposal of Prof V. A. Vanyukov to work with highly siliceous manganese slags had not yet been fully put into practice. The work was continued in 1935 at the Karsakpay plant by D. I. Lisovskiy, I. I. Ivanov, and I. I. Surovov with the cooperation of Engineer I. A. Strigin.

Experiments in adding manganous oxide on a plant scale were carried out in August and September 1935. It was added in such quantity that the slag would

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contain 2 - 3 percent MnO. Average composition of the slag was 51 - 55 percent SiO₂, 11 - 13 percent Al₂O₃, 13 - 18 percent Fe, 3 - 4 percent CaO, and 1.6 - 2.5 percent MnO.

In the course of these 2 months it was shown that slag containing 2 percent MnO was sufficiently fluid, even at the comparatively low temperature of the reverberatory furnace. Slags resulting in obtaining 54 percent matte containing 0.3 percent Cu. The difficulty of obtaining manganese ore hindered smelting at the Karsakpay plant until 1945, when Dzhezkazgan manganese ore began to be mined for use in ferrous metallurgy. A wide-gauge road was built to the mines.

Smelting to yield slags containing 35 - 38 percent SiO₂ and copper mattes containing 25 - 28 percent Cu was begun at Balkhash in 1938. In 1942 and 1943, acid slags and rich matte were introduced there. In these years, smelting was carried on with a lime flux to yield slag containing 51 - 54 percent SiO₂ and matte containing 38 - 42 percent Cu. Recovery of 92 - 93 percent Cu was attained. Addition of manganese-containing fluxes has not as yet been introduced.

Laboratory tests have shown that the presence of 1.5 - 2 percent manganous oxide makes slag mobile and fluid, so that the slag may contain as much as 54 - 57 percent silica. Its presence also cuts copper losses.

Conclusions

The proposal made by the author in 1927 - 1928 to the Atbasar Trust, namely, to carry on smelting so as to yield highly siliceous manganese slag and rich matte, was not accepted and introduced at once. The planning organizations, plant engineering, and technical personnel did not put this proposal into practice for a considerable length of time.

The resolution of the third session of the Scientific Council of the Kazakhstan Section of the Academy of Sciences of the USSR, devoted to the problems of Bolshoy Altay and Bolshoy Dzhezkazgan combines, was the turning point.

From 1943 to 1945 were years of fruition for the many years of work by Prof V. A. Vanyukov and his students in the processing field. These years brought the introduction of his method of treating Central Kazakhstan ores and concentrates, and the following culminating events:

1. The experience accumulated in the practical work of the Karsakpay and Balkhash Copper Smelting Plants was generalized.
2. The effect of additions to the charge for reducing the viscosity of highly siliceous slags was studied by F. M. Loskutov and K. S. Ponomarev and their findings published in K Voprosu Izucheniya Plavkosti i Vyazkosti Shlakov Balkhashskogo Medeplyavil'nogo Zavoda (The Problem of the Fusibility and Viscosity of Slags at the Balkhash Copper Smelting Plant).
3. Lime flux replaced iron ore at the Balkhash plant.
4. The Karsakpay plant introduced a manganese flux in the form of Dzhezkazgan manganese mine tailings.

Therefore, the following may be considered as having been scientifically and practically demonstrated and proved:

1. That it is expedient and economical to carry on smelting of Central Kazakhstan ores and concentrates so as to yield highly siliceous slags, containing manganous oxide, and rich mattes. See Tsvetnyye Metally (Nonferrous Metals), 1944, No 3 - 4, p 34.

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2. That this method, while making use of the properties of the ores and concentrates being smelted, reduces flux requirements many times and completely eliminates the need for sulfurizing additions.

3. That adding manganese-ore tailings to the charge reduces the viscosity and the melting point of acid slags and increases the fusibility of ores and concentrates.

4. That smelting to yield acid slags containing manganous oxide, a limited amount of alumina, and a small amount of ferrous oxide (no iron ore added) raises the possibility of having only about 0.2 - 0.3 percent Cu in the waste slag and of recovering up to 98.5 percent Cu in the process of reverberatory smelting.

5. That the amount of waste slag is reduced two to three times.

6. That the copper-containing materials form a great portion of the charge and that this fact makes for their economically profitable treatment.

[Appended figures follow.]

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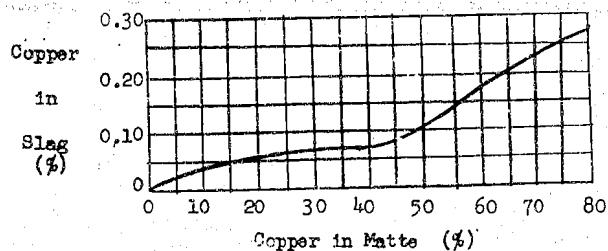


Figure 1. Copper Loss in Slag in Relation to Copper Content in Matte

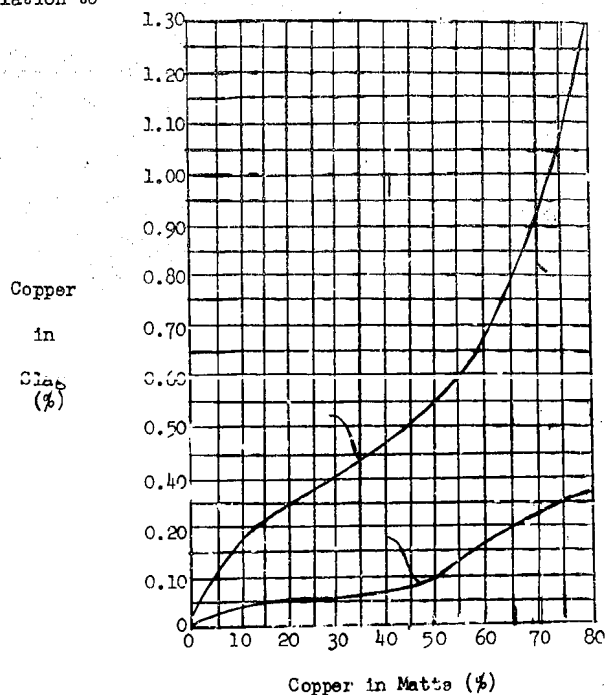


Figure 2. Copper Loss in Slag in relation to Copper Content in Matte /note omission of 0.30/

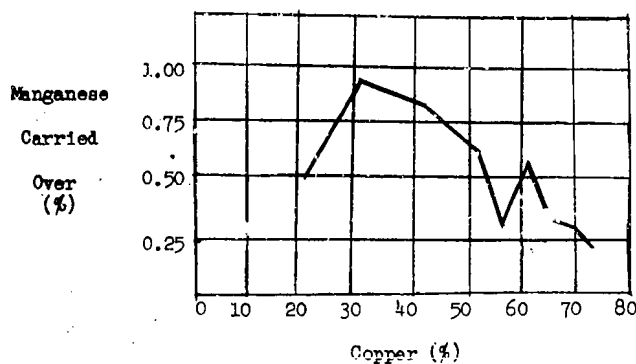


Figure 3. Manganese Carried Over into Matte, in Relation to Copper Content

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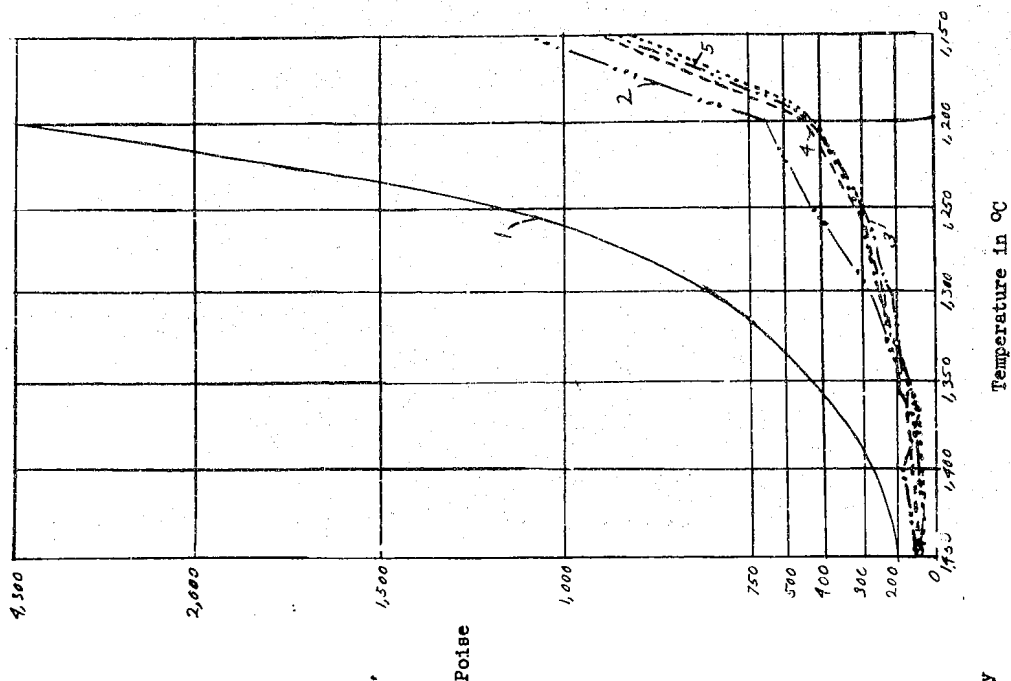


Figure 5. Effect of Temperature on Viscosity of Slag of Second Group

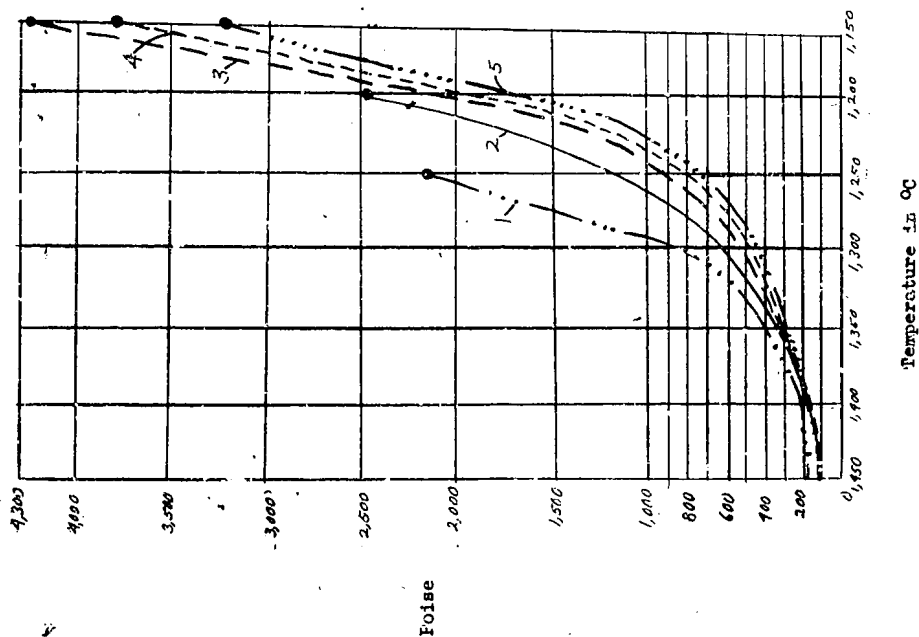


Figure 4. Effect of Temperature on Viscosity of Highly Siliceous Slag of First Group

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